Thermodynamics of Ternary Alcohol -Saturated Hydrocarbon Mixtures

Sonderdruck: „Zeitschrift für Physikalische Chemie Neue Folge", 85 (1973) 241–248
Herausgegeben von G. Briegleb, Th. Förster, W. Jaenicke, G.-M. Schwab, E. Wicke
Akademische Verlagsgesellschaft, Frankfurt am Main

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By

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With 3 figures

(Received September 25, 1972)

Abstract

A theory is presented to predict the excess thermodynamic functions of ternary mixtures including one alcohol and two saturated hydrocarbons from binary data. The one-parameter Flory-Huggins equation is applied to describe the excess Gibbs free energy data of binary hydrocarbon mixtures with physical and size effects. The Kretschmer-Wiebe equation is used for alcohol-saturated hydrocarbon mixtures having physical and strong chemical interactions. The two equations are combined to derive expressions for the excess Gibbs free energy, the excess enthalpy of mixing, and the excess heat capacity data on a ternary alcohol-saturated hydrocarbon mixture. Prediction is shown to be successful for these three thermodynamic functions of the ethanol-cyclohexane-*n*-heptane system.

Introduction

The Kretschmer-Wiebe equation[1] proposed to treat binary alcohol-inert hydrocarbon mixtures has been compared with experimental excess Gibbs free energy and enthalpy of mixing for 11 binary systems by H. RENON and J. M. PRAUSNITZ[2]. They concluded that in spite of its simplifying assumption, the Kretschmer-Wiebe equation of associated solutions gives a good representation of the properties of concentrated solutions of alcohols in saturated hydrocarbons. Further

[1] C. B. KRETSCHMER and R. WIEBE, J. chem. Physics 22 (1954) 1697.
[2] H. RENON and J. M. PRAUSNITZ, Chem. Eng. Sci. 22 (1967) 299.

studies on the Kretschmer-Wiebe equation have been published by H. KEHIAIAN and A. TRESZCZANOWICZ[3-6].

This work presents an extension of the Kretschmer-Wiebe equation to ternary systems including one alcohol and two hydrocarbons to predict the excess thermodynamic functions of the systems from only binary data.

Derivation of equations

The fundamental assumptions concerning the associated model are listed as follows.

1. The alcohol molecules (A) presented in the solution form successively linear, hydrogen bonded i-mers. Thus $A_1 + A_i = A_{i+1}$.

2. The association constant of the above reaction does not concern i.

3. There is no volume change of mixing.

4. The enthalpy of formation of a hydrogen bond is independent of the temperature and the degree of association.

We consider one stoichiometric mole of an alcohol-hydrocarbon mixture containing x_a moles of alcohol, x_b moles of hydrocarbon B, and x_c moles of hydrocarbon C. The alcohol consists of n_1 moles of monomer, n_2 moles of dimer, . . . , n_i moles of i-mer.

The Flory-Huggins equation[7] for the Gibbs free energy of mixing alcohol and hydrocarbons is expressed by

$$\frac{g^M}{RT} = \sum_{i=1}^{\infty} n_i \ln \varphi_i + x_b \ln \varphi_b + x_c \ln \varphi_c + \frac{(x_a v_a + x_b v_b + x_c v_c)(\beta_{ab} \varphi_a \varphi_b + \beta_{ac} \varphi_a \varphi_c + \beta_{bc} \varphi_b \varphi_c)}{RT} \quad (1)$$

where φ is the volume fraction, β is the physical interaction parameter, and the subscripts a, b, and c represent alcohol and hydrocarbons,

[3] H. KEHIAIAN and A. TRESZCZANOWICZ, Bull. Soc. chim. France (1969) 1561.

[4] H. KEHIAIAN and A. TRESZCZANOWICZ, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 18 (1970) 693.

[5] A. TRESZCZANOWICZ and H. KEHIAIAN, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 18 (1970) 723.

[6] A. TRESZCZANOWICZ and H. KEHIAIAN, Bull. Acad. Polon. Sci., Ser. Sci. Chim. 18 (1970) 729.

[7] J. H. HILDEBRAND, J. M. PRAUSNITZ and R. L. SCOTT, Regular and Related Solutions, Van Nostrand-Reinhold, New York 1970.

respectively. The chemical potentials obtained by differentiating Eq. (1) with respect to the number of moles of each species are

$$\mu_i - \mu_i^0 = RT\left(\ln \varphi_i + 1 - \frac{v_i}{V}\right) + v_i\,[\beta_{ab}\,(\varphi_b^2 + \varphi_b\,\varphi_c) + \beta_{ac}\,(\varphi_b\,\varphi_c + \varphi_c^2) - \beta_{bc}\,\varphi_b\,\varphi_c] \tag{2}$$

$$\mu_b - \mu_b^0 = RT\left(\ln \varphi_b + 1 - \frac{v_b}{V}\right) + v_b\,[\beta_{bc}\,(\varphi_c^2 + \varphi_c\,\varphi_a) + \beta_{ab}\,(\varphi_c\,\varphi_a + \varphi_a^2) - \beta_{ac}\,\varphi_c\,\varphi_a] \tag{3}$$

$$\mu_c - \mu_c^0 = RT\left(\ln \varphi_c + 1 - \frac{v_c}{V}\right) + v_c\,[\beta_{ac}\,(\varphi_a^2 + \varphi_a\,\varphi_b) + \beta_{bc}\,(\varphi_a\,\varphi_b + \varphi_b^2) - \beta_{ab}\,\varphi_a\,\varphi_b] \tag{4}$$

where V is the volume of one true mole of solution, v is the molar volume of species and the superscript o represents the property of pure component.

$$\frac{1}{V} = \sum_{i=1}^{\infty} \frac{\varphi_i}{v_i} + \frac{\varphi_b}{v_b} + \frac{\varphi_c}{v_c}. \tag{5}$$

For equilibrium on the alcohol i-mer forming reaction

$$A_i + A_1 = A_{i+1}. \tag{6}$$

We define the chemical equilibrium constant by

$$K = \frac{C_{i+1}}{C_i\,C_1\,v_a} = \frac{\varphi_{i+1}}{\varphi_i\,\varphi_1}\,\frac{i}{i+1} \tag{7}$$

where C represents the concentration.

From Eq. (7) we have

$$\varphi_a = \sum_{i=1}^{\infty} \varphi_i = \frac{\varphi_1}{(1 - K\varphi_1)^2} \tag{8}$$

$$\frac{1}{V} = \frac{\varphi_a\,(1 - K\varphi_1)}{v_a} + \frac{\varphi_b}{v_b} + \frac{\varphi_c}{v_c}. \tag{9}$$

According to PRIGOGINE[8] the chemical potential of the stoichiometric alcohol component is equal to that of the alcohol monomer.

$$\mu_a = \mu_1. \tag{10}$$

[8] I. PRIGOGINE and R. DEFAY, Chemical Thermodynamics, Wiley, New York 1954.

Then

$$\mu_a - \mu_a^0 = RT\left(\ln\frac{\varphi_1}{\varphi_1^0} - \frac{v_1}{V} + \frac{v_1}{V^0}\right) + v_1[\beta_{ab}(\varphi_b^2 + \varphi_b\varphi_c) + \beta_{ac}(\varphi_b\varphi_c + \varphi_c^2) - \beta_{bc}\varphi_b\varphi_c]. \tag{11}$$

φ_1, φ_1^0, and $1/V^0$ are, respectively, given by

$$\varphi_1 = \frac{1 + 2K\varphi_a - \sqrt{1 + 4K\varphi_a}}{2K^2\varphi_a} \tag{12}$$

$$\varphi_1^0 = \frac{1 + 2K - \sqrt{1 + 4K}}{2K^2} \tag{13}$$

$$\frac{1}{V^0} = \frac{(1 - K\varphi_1^0)}{v_a}. \tag{14}$$

The excess Gibbs free energy is represented as follows:

$$g^E = RT(x_a \ln\gamma_a + x_b \ln\gamma_b + x_c \ln\gamma_c) = RT\left[x_a \ln\frac{\varphi_1}{\varphi_1^0 x_a} + x_b \ln\frac{\varphi_b}{x_b} + x_c \ln\frac{\varphi_c}{x_c} + \frac{x_a v_a}{V^0} - \frac{(x_a v_a + x_b v_b + x_c v_c)}{V}\right] + (x_a v_a + x_b v_b + x_c v_c)(\beta_{ab}\varphi_a\varphi_b + \beta_{ac}\varphi_a\varphi_c + \beta_{bc}\varphi_b\varphi_c). \tag{15}$$

The enthalpy of formation of the solution is

$$H = h_a \sum_{i=1}^{\infty}(i-1)n_i + (x_a v_a + x_b v_b + x_c v_c)(\beta'_{ab}\varphi_a\varphi_b + \beta'_{ac}\varphi_a\varphi_c + \beta'_{bc}\varphi_b\varphi_c) \tag{16}$$

where h_a is the enthalpy of a hydrogen bond formation.

The definition of excess enthalpy gives

$$h^E = H - x_a H^0 = h_a x_a K(\varphi_1 - \varphi_1^0) + (x_a v_a + x_b v_b + x_c v_c)(\beta'_{ab}\varphi_a\varphi_b + \beta'_{ac}\varphi_a\varphi_c + \beta'_{bc}\varphi_b\varphi_c) \tag{17}$$

where H^0 is the value of H for pure alcohol.

$$\beta' = \beta - T\frac{d\beta}{dT}. \tag{18}$$

The excess heat capacity $c_p{}^E$ is obtained by differentiating h^E with respect to temperature.

$$c_p{}^E = \left[\frac{\partial h^E}{\partial T}\right]_{p,x}$$
$$= R\left[\left(\frac{h_a}{RT}\right)^2\left(\frac{1-K\varphi_1}{1+K\varphi^1}\varphi_1 - \frac{1-K\varphi_1{}^0}{1+K\varphi_1{}^0}\varphi^0{}_1\right) + \frac{\Delta c_p{}^0}{R}(\varphi_1 - \varphi_1{}^0)\right]Kx_a$$
$$+ (x_a v_a + x_b v_b + x_c v_c)\,(\beta''_{ab}\varphi_a\varphi_b + \beta''_{ac}\varphi_a\varphi_c + \beta''_{bc}\varphi_b\varphi_c) \qquad (19)$$

where $\Delta c_p{}^0 = \frac{\partial h_a}{\partial T}$ and this value is zero in this work.

$$\beta'' = \frac{\partial \beta'}{\partial T}. \qquad (20)$$

Determination of Parameters from Binary g^E, h^E, and $c_p{}^E$ Data

A least squares fitting program was used to obtain the best value of each parameter in the curve fitting of three excess thermodynamic

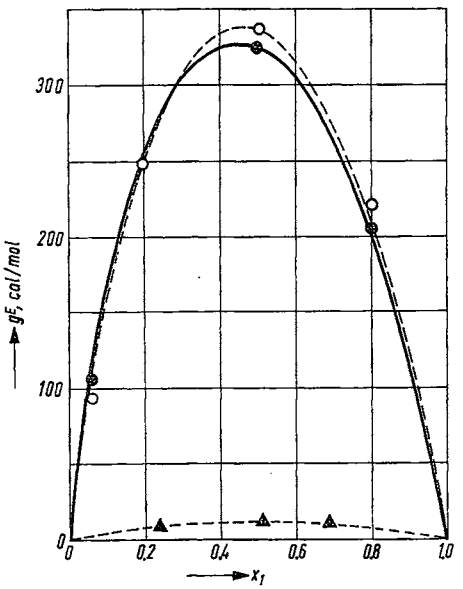

Fig. 1. g^E vs. liquid mole fraction diagram

○ Exptl. ———— Calc. ethanol(1)-cyclohexane(2) Ref.[9]
● Exptl. ———— Calc. ethanol(1)-*n*-heptane(2) Ref.[9]
▲ Exptl. ---------- Calc. cyclohexane(1)-*n*-heptane(2) Ref.[10]

[9] I. Klesper, Z. physik. Chem. Neue Folge **51** (1966) 1.

[10] H. Grosse-Wortmann, W. Jost and H. Gg. Wagner, Z. physik. Chem. Neue Folge **49** (1966) 74.

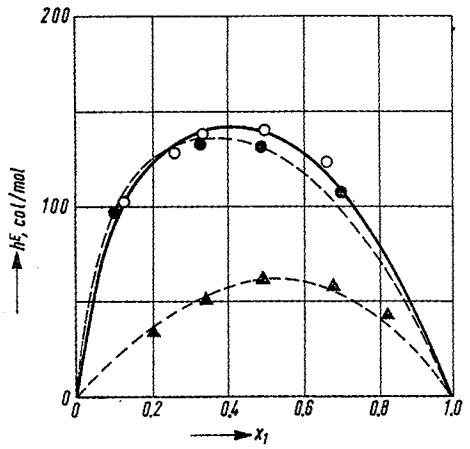

Fig. 2. h^E vs. liquid mole fraction diagram

○ Exptl. ———— Calc. ethanol(1)-cyclohexane(2) Ref.[10]
● Exptl. — — — — — Calc. ethanol(1)-*n*-heptane(2) Ref.[10]
▲ Exptl. ····· Calc. cyclohexane(1)-*n*-heptane(2) Ref.[10]

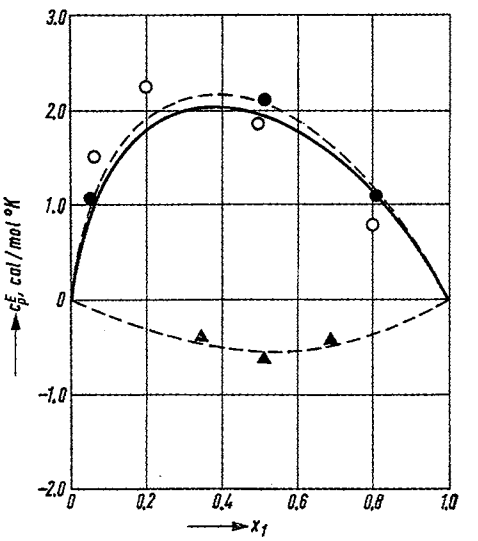

Fig. 3. c_p^E vs. liquid mole fraction diagram

○ Exptl. ———— Calc. ethanol(1)-cyclohexane(2) Ref.[9]
● Exptl. — — — — — Calc. ethanol(1)-*n*-heptane(2) Ref.[9]
▲ Exptl. ····· Calc. cyclohexane(1)-*n*-heptane(2) Ref.[10]

properties versus composition. The program minimized the sum
the squares of difference between experimental and calculated the
modynamic properties over the whole concentration range. In th

Table 1. *Binary parameters at 20 °C and absolute arithmetic mean deviations*

System	No. of data points			Parameter			Absolute arithmetic mean deviation			Data source		
	g^E	h^E	$c_p{}^E$	β (cal/cc)	β' (cal/cc)	β'' (cal/cc °K)	g^E (cal/mol)	h^E (cal/mol)	$c_p{}^E$ (cal/mol °K)	g^E	h^E	$c_p{}^E$
Ethanol-cyclohexane	4	5	4	3.490	2.822	0.028	4.14	2.78	0.37	9	10	9
Ethanol-*n*-heptane	4	5	4	2.653	1.049	0.013	3.61	4.54	0.18	9	10	9
Cyclohexane-*n*-heptane	3	5	4	0.578	1.998	−0.017	0.19	3.18	0.08	10	10	10

Table 2. *Predicted results for the thermodynamic functions of the ethanol(1)-cyclohexane(2)-n-heptane(3) system at 20 °C*

x_1	x_2	g^E	Δ(I)	h^E	Δ(I)	Δ(II)	$c_p{}^E$	Δ(I)	Δ(II)
		(cal/mol)		(cal/mol)			(cal/mol °K)		
0.3303	0.3204	315.58	−5.07	166.73	−5.10	4.25	1.99	0.19	−0.04
0.5978	0.2019	316.97	−0.53	142.13	2.94	3.68	1.61	−0.10	−0.00
0.2534	0.3957	285.97	−3.95	166.79	−5.04	4.89	1.91	0.27	−0.12
0.2003	0.6006	250.79	−5.98	157.31	−1.24	4.01	1.63	0.11	−0.34
0.4059	0.1962	332.27	−4.60	158.21	−4.59	2.80	2.07	0.15	−0.04
0.3997	0.4013	327.30	−6.01	164.58	−2.49	4.13	1.93	0.07	0.12
0.2046	0.1997	257.35	−2.85	148.81	−6.98	3.00	1.91	0.26	−0.11
Absolute arithmetic mean deviation =		4.14			4.05	3.82		0.16	0.11

Δ = Experimental value − calculated value. I = This work. II = H. Grosse-Wortmann, W. Jost and H. Gg. Wagner.

paper, K for ethanol is 190 at 50 °C and h_a is −6.0 kcal/mol as proposed by H. RENON and J. M. PRAUSNITZ[2]. The temperature dependence of K is fixed according to the van't Hoff relation.

$$\frac{d \ln K}{d (1/T)} = -\frac{h_a}{R}. \tag{21}$$

Table 1 shows the numerical values of parameters obtained and the absolute arithmetic mean deviations of calculated values from experimental data[9,10] for three binary systems. The calculated values are compared with the experimental data in Figs. 1, 2, and 3. Although the calculated c_p^E curve for the ethanol-cyclohexane system does not represent well the very skewed experimental data, the other calculated values are generally in good agreement with the experimental results.

Prediction of ternary g^E, h^E, and c_p^E data

Table 2 shows the difference between experimental and calculated values of three thermodynamic excess functions for the ethanol-cyclohexane-*n*-heptane mixtures[10]. Prediction seems to be successful. The table also lists the difference obtained by H. GROSSE-WORTMANN, W. JOST and H. GG. WAGNER[10] using the following equation

$$h^E_{123} = x_1 x_2 \Sigma A^v_{12} (2x_1 - 1)^v + x_1 x_3 \Sigma A^v_{13} (2x_1 - 1)^v + x_2 x_3 \Sigma A^v_{23} (x_2 - x_3)^v. \tag{22}$$

Eq. (22) is entirely empirical, but the present approach has a sound theoretical background.

Acknowledgement

The author thanks the Computer Center, Osaka University, and the Data Processing Center, Kyoto University, for the use of their facilities.